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Quantitative Determination of Absolute Organohalogen Concentrations in Environmental Samples by X-ray Absorption Spectroscopy

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A method for quantification of organic and inorganic halogen concentrations in environmental samples using x-ray absorption spectroscopy has been developed. Organochlorine (Cl_{org}) and inorganic chloride (Cl_{inorg}) concentrations are determined from Cl 1s XANES spectra. The absolute fluorescence intensity of these spectra is linearly dependent on Cl concentration. Calibration curves are obtained from NaCl standards in a matrix of uniform bulk density, and Cl concentration in natural samples is estimated from these curves with high precision. The fractions of Cl_{inorg} and aliphatic/aromatic Cl_{org} contributing to the total Cl 1s XANES signal are computed through least-squares spectral fitting with representative model compounds. Concentrations of organic and inorganic Br (Br_{org} and Br_{inorg}) in sediment samples are also measured using a combination of XRF and Br 1s XANES spectroscopy.

Halogens undergo complex biogeochemical transformations in terrestrial systems, cycling between organic and inorganic forms. Naturally produced organohalogens include a diverse array of relatively low molecular weight molecules, as well as macromolecules of indeterminate structure. Despite the ubiquity of natural organohalogens, the processes associated with their formation and degradation in the environment remain poorly understood, largely due to the inadequacy of available techniques to account for the myriad halogen species in heterogeneous soil, sediment, plant, and aqueous samples. Established quantitative methods require chemical isolation of organohalogen fractions from natural samples and are prone to partial recoveries and/or chemical alterations of halogens. We have applied synchrotron-based x-ray fluorescence (XRF) and x-ray absorption near-edge structure (XANES) spectroscopy to the *in situ* determination of Cl_{org} and Br_{org} concentrations in natural samples.

Quantification of Cl relies on the absolute fluorescence intensity of Cl 1*s* XANES spectra (acquired at beamline X19A) determined at 2850.8 eV, an energy ~20 eV above the Cl K-absorption edge (**Figure 1A**). By this energy, the near-edge oscillations are attenuated and absorption intensity is independent of Cl speciation. Polyacrylic acid-based NaCl standards yield calibration curves with a strong linear relationship between Cl concentration and absolute Cl fluorescence intensity (**Figure 1B**). X-ray beam absorption and scattering by polyacrylic acid-based standards and natural organic matter (NOM) are comparable, allowing for direct measurement of Cl concentrations in homogenized NOM sample pellets, which minimizes matrix effects.

Graduate student author Alessandra Leri (left) and Michael Hay (right) collect natural organic matter samples in the field.

Unnormalized Cl 1*s* XANES spectra of oak leaf NOM at progressive stages of decay are shown in **Figure 2A** (a = least degraded; c = most degraded). Comparison of the absolute Cl fluorescence intensity values of these spectra with standard curves (as in **Figure 1B**) yields the following total Cl concentrations: a, 364 ppm; b, 141 ppm; c, 70 ppm. The decreasing trend in Cl concentration is consistent with leaching of soluble forms of Cl from the mulch material as part

of the degradation process.

In addition to providing Cl concentration measurements, Cl 1*s* XANES spectra illuminate the chemical forms of Cl present in a sample. Cl_{inorg} exhibits a broad absorption maximum (**Figure 2B, x**) higher in energy than the more intense maxima characteristic of Cl_{org} compounds. These sharp peaks denote 1s → π* or σ* transitions and differ in energy depending on C-Cl bond length, as becomes evident through comparison of aliphatic and aromatic Cl_{org} spectra **(Figure 2B, y-z)**. The substantial variations in spectral features depending on the coordination environment of Cl allow percentage estimates of Cl_{inorg} and aliphatic and aromatic Cl_{org} in natural samples to be ascertained via least-squares fitting of normalized sample spectra with spectra of representative model compounds (**Figure 2B**). Combination of these proportions with total Cl concentrations yields the concentrations of Cl_{inorg}, aromatic Cl_{org}, and aliphatic Cl_{org} in NOM samples (**Figure 2, caption**).

Total Br concentrations in environmental samples have been determined via XRF analysis for decades. The novelty of our application lies in the combination of quantitative information from XRF (acquired at beamline X26A) with Br speciation information from Br 1*s* XANES spectra (acquired at beamline X23A2) to determine absolute concentrations of Br_{org} and Br_{inorg} in chemically heterogeneous sediments.

This method provides a rigorous new approach to the determination of organohalogen concentrations in complex natural samples *in situ*. Robust, quantitative information about organohalogen fluxes in soil and sediment systems will help complete the description of natural halogen cycles, potentially illuminating the sources and sinks of naturally and industrially produced organohalogens in the environment.

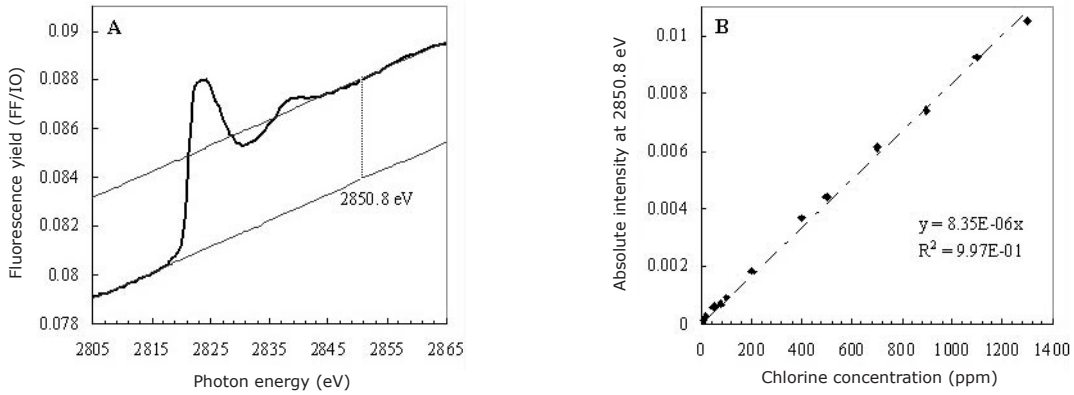

Figure 1. *Quantification of Cl concentration from Cl 1s XANES spectra. A) Unnormalized Cl 1s XANES spectrum of NaCl standard in PAA matrix (200 ppm Cl). The difference at 2850.8 eV between splines through the pre-edge and post-edge regions is used as a measure of absolute Cl fluorescence intensity. B) Relationship between Cl concentration in PAA-based NaCl standards and absolute Cl fluorescence intensity. Dashed line, equation, and R^2 value represent linear fits to the data.*

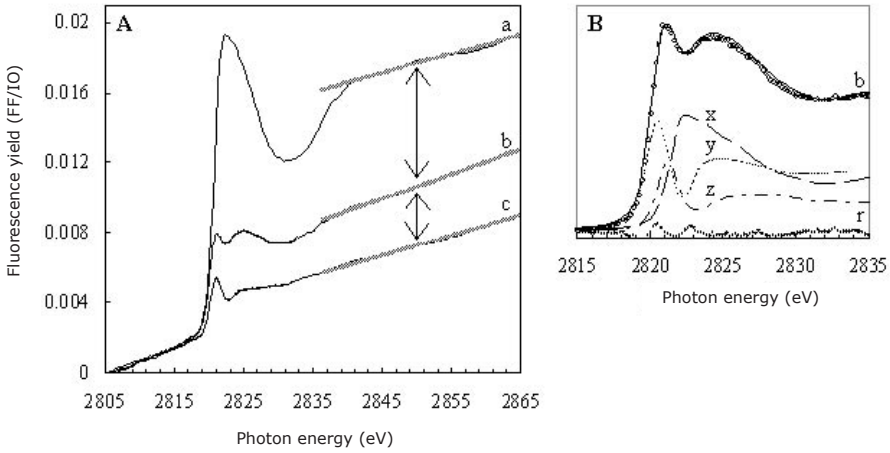

Figure 2. *Determination of Cl speciation and concentration in NOM samples from Cl 1s XANES spectra. A) Unnormalized Cl 1s XANES spectra of pulverized oak leaves at different stages of decay (a = least degraded; b = more degraded; c = most degraded). Arrows illustrate the differences in absolute Cl fluorescence intensity among the spectra. B) Least-squares fit of background-subtracted, normalized spectrum b with representative inorganic (x, glycine-HCl), aliphatic (y, chlorodecane), and aromatic (z, chlorophenol red) Cl model compounds. Spectrum b data are represented by circles and fit by the solid line; r is the residual after the fit. Estimated Cl speciation by least-squares fitting: a, 78% inorganic (284 ppm), 16% aromatic (58 ppm), 6% aliphatic (22 ppm); b, 40% inorganic (56 ppm), 20% aromatic (29 ppm), 40% aliphatic (56 ppm); c, 16% inorganic (12 ppm), 42% aromatic (29 ppm), 42% aliphatic (29 ppm).*